CHAPTER XXVIII

REFINING OF MAGNESIUM

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105. Impurities in Industrial Magnesium

Magnesium, freshly removed from the bath, usually contains impurities which make it unsuitable for immediate use. For that reason crude magnesium first needs to be purged of those impurities – it needs refining.

The impurities contained by the crude magnesium are divided into the following three groups: 1) Metallic impurities picked up by the magnesium during its electrolytic separation from the raw-material and from the components except $MgCl_2$ of the electrolyte; 2) Non-metallic impurities, mechanically adhering to the magnesium as it is removed from the bath; 3) Impurities appearing in magnesium as a result of its chemical reaction with gases and tank-lining materials.

To the first group of impurities belong both iron and aluminum as well as potassium and sodium. Iron and aluminum are components of the electrolyte and, being more electro-positive than magnesium, readily deposit on the cathode under ordinary conditions of the process. As far as potassium and sodium are concerned, these appear in magnesium in greater quantities for a low concentration of $MgCl_2$ in the electrolyte or for an increased cathodic density of the current.

To the second group of impurities belong those mechanically adhering to the metal being scooped out from the bath tank: $MgCl_2$, KCl, NaCl and MgO. This kind of impurity, $MgCl_2$ in particular, shows a very strong destructive action on crude magnesium during storage. Due to the hygroscopic nature of magnesium chloride, moisture and HCl [formed by hydrolysis] appear on the surface of the magnesium ingot, rapidly corroding the metal.

To the third group of impurities belong: Nitride resulting from the reaction of magnesium with atmospheric nitrogen; hydride, a compound of

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magnesium and hydrogen; carbide, formed by reaction of magnesium with the carbon lining of the tank; and finally, silicide [magnesium silicide], resulting from an interaction of the metallic magnesium with silica.

The crude magnesium, scooped out of the bath, usually has the following approximate percentages of impurities: Chlorides, 2-3 percent; Iron up to 0.1 percent; Magnesium carbide up to 0.05 percent; Magnesium silicide up to 0.6 percent; and Potassium plus Sodium, 0.2 percent. The metallic magnesium, offered on the market, should have an extremely low content of impurities, and according to the regulation OST 10032 - 38, dated 28 April 1938, two brands are to be distinguished: M 1 and M 2, depending on their purity (Table 82).

Refining of the crude magnesium can be accomplished by various methods; but the two most important are: 1) Refining by smelting with fluxes, and 2) Refining by sublimation (distillation).

The first method makes possible the purging from metals of the chief non-metallic impurities and mechanical admixtures. The second method yields magnesium of a very high grade of purity, at the same time cleansing it almost completely of the metallic admixtures.

106. Refining of Magnesium by Smelting with Fluxes

Refining of magnesium by smelting with fluxes is the method most widely used in plant practice. By this process the crude magnesium, scooped from the bath, is smelted with fluxes mainly of several chlorine and fluorine salts.

TABLE 82

CLASSIFICATION OF MAGNESIUM ACCORDING TO OST 10032 - 38

Formula	Mg not less than	Fe	Cl	Na	K	Al	Si	Others	Total Impurities
		not more than							
M 1	99.85	0.04	0.005	0.1	0.005	0.05	0.04	0.045	0.15
M 2	99.50	0.05	0.01	-	-	0.100	0.30	0.24	0.50

(1) Industrial application of M 1: For casting and machining; for producing reliable alloys of magnesium, obtained by casting and pressure machining, including the semifinished products made of these alloys; for special pyrotechnics.

(2) M 2 is used as the starting material for producing regular alloys of magnesium, obtained by casting or pressure machining, including the semi-finished products made of those alloys; for general pyrotechnics, photography, chemical industry etc.

The purpose of the fluxes is first, to protect magnesium from any contact with the air during smelting, and, second, to remove impurities contained in crude magnesium by dissolving or slagging.

The number of fluxes offered and used in practice is very large. The most important flux component is anhydrous magnesium chloride which, by reacting chemically with such impurities as metallic sodium, potassium, and magnesium nitride removes them from the crude magnesium.

Other chlorine salts present in the fluxes are KCl and NaCl.

In order to eliminate the oxides (MgO, SiO_2) from magnesium, a mixture of fluorine salts is also added to the fluxes. CaF_2, NaF and AlF_3 are most commonly used. The admixtures of the magnesium oxide are dissolved in fluorine salts; the silica, on the other hand, forms a volatile compound with fluorine (SiF_4) which is eliminated during magnesium refining.

For example, the following flux compound, used for magnesium refining has:

55 percent $MgCl_2$; 12 percent KCl; 4.5 percent CaF_2; 5 percent NaF; 10 percent $CaCl_2$; 12 percent MgO and 1.5 percent SO_4.

The refining process of magnesium with fluxes is usually carried on in electrical crucible furnaces. A small amount of flux and crude magnesium are put into a preheated crucible. As these melt, new portions of flux and crude magnesium are added little by little until the crucible is full.

After this the furnace temperature is elevated to 700 degrees [Centigrade] and the metal mixed by a stirrer for 0.5-1 hour with the flux.

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Then the slag formed is removed from the surface of the fused mass and a special high melting flux (melting point 1000 degrees), called a thickener, is poured in. Its purpose is to form a thick scum over the metal and thereby prevent access of air to the metal.

Next, to ease the rise of impurities to the surface, the temperature of the metal is increased to 800-850 degrees and then the furnace is cooled to 670 degrees. An opening is then made in the scum and the refined magnesium allowed to run into ingot molds.

Finally, in order to cleanse the surface of the cast metal from any adhering slag, the ingots are temporarily subjected to corrosion by a weak solution of nitric acid. After washing in hot water and drying, the magnesium ingot is stored.

Magnesium lost in the series of fusing processes amounts to 5 percent. Flux loss is 0.05 ton per ton of magnesium and electric power consumption is about 950 kilowatt hours per ton of magnesium.

107. Refining of Magnesium by Sublimation

In this process of refining of magnesium, the high vapor pressure of this metal, even at temperatures below the melting point (Table 83) is utilized.

This technique of refining magnesium can be accomplished either by sublimation, i.e. at a temperature below its melting point, or by distillation, i.e. at the temperature above its melting point. In either case the vapor pressure of magnesium at the given temperature can be raised /relative to air whose pressure is lowered/ if we perform this process in a vacuum.

TABLE 83

VAPOR TENSION OF MAGNESIUM AND OTHER METALS

(According to Johnston)

Metal	Melting Point °C	Vapor Tension of Metals in MM of Mercury Column at Different Temperature °C							
		0.001	0.01	0.1	1.00	10.0	50.0	100.0	300
Zn	419	290	350	420	500	610	700	750	900

Metal	Melting Point °C	Vapor Tension of Metals in MM of Mercury Column at Different Temperature °C							
		0.001	0.01	0.1	1.00	10.0	50.0	100.0	300
Mg	651	380	440	520	620	750	860	920	1120
Al	657	730	830	950	1090	1280	1440	1520	1850
Mn	1225	790	890	1020	1170	1360	1530	1610	1900
Cu	1083	1080	1200	1340	1520	1740	1930	2030	2250
Fe	1520	1130	1250	1400	1500	1820	2010	2110	2420

According to their vapor pressure, the impurities contained in the crude magnesium can be divided into following two groups:

1) Impurities with a greater vapor pressure than that of magnesium; to these impurities belong occluded chlorides ($MgCl_2$, KCl and NaCl) and alkaline metals which sublimate more easily than magnesium;

2) Impurities of a lower vapor pressure than magnesium. To these impurities belong: Iron, silicon, manganese, copper, and other metals which, as compared with magnesium, sublimate only slightly.

Thus, in the course of refining magnesium by sublimation or distillation, an elimination from magnesium first of all impurities of higher volatility, and afterwards, of all impurities of lower volatility is accomplished.

Refining of magnesium by sublimation is usually performed under vacuum. The apparatus (Figure 200) usually consists of a steel retort provided with a tightly covering lid (1). The lower part of the retort is inserted into a nichrome heater (2), its upper part being exposed to the air, thus making the condensation of the vaporized magnesium easier.

The magnesium to be refined is put on the floor of the retort (3). The sublimed magnesium in crystal form (druse) deposits on the inner shell of the cylindrical condenser (4) made of sheet iron and placed inside the retort. By means of a vacuum pump the air inside the retort is exhausted.

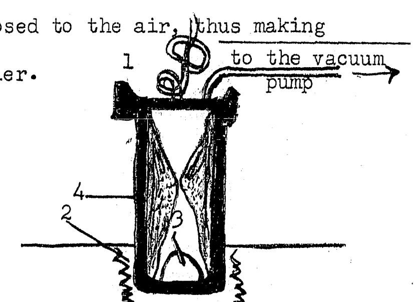

Figure 200. Sketch of a retort for refining of magnesium by sublimation.

After accumulation of the crystals of the sublimed magnesium on the shell of the condenser, the retort is cooled, and the condenser replaced by another one.

The druses of the sublimed magnesium are now separated from the condenser shell, melted and poured into ingots.

It is necessary to note that the magnesium deposited on the condenser is not quite uniform and still contains impurities. Accordingly, the sublimate can be divided into a few vertical zones.

The upper zone consists of very small crystals which quickly darken upon exposure to the air. This part of the sublimate contains nearly all (up to 85 percent) the highly volatile impurities of the crude magnesium: Potassium, sodium and magnesium chlorides. The remainder of this zone contains 1-2 percent Na.

The second zone consists of larger crystals of magnesium, having few impurities.

The next zone of the sublimate represents the purest magnesium and consists of still larger crystals. The magnesium of this zone shows an exceedingly high resistance to corrosion.

The last and lowest zone consists of fine crystals of magnesium containing impurities of low volatility (iron, silicon).

The zone of the purest magnesium contains approximately 80 percent of the entire sublimate.

The metal of the less pure zones is subjected to another sublimation. Experience has proved that the best temperature of sublimation of magnesium is 580-600 degrees [Centigrade] and the temperature of the condensation zone of the purest magnesium should be within the limits of 450-500 degrees. Pressure inside the evacuated retort (residual pressure) registers 0.1-0.2 millimeters of mercury. The sublimed magnesium, obtained in this way has a very high purity and contains: 0.01-0.02 percent Al; 0.001-0.002 percent Si; 0.005 percent Fe; 0.01 percent KCl +NaCl and 99.96 percent Mg.

Besides crude magnesium, waste magnesium and its alloys, secondary magnesium, as well as alloys of magnesium with heavy metals obtained e. g. immediately by electrolysis (see section 104), can be refined by sublimation.